

Infrared Interferometry - Emission Spectra in the Sodium Chloride Region

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Introduction

Spawned primarily by the space industry, ⁽¹⁾ infrared interferometry is a relatively new technique to the practicing spectroscopist. Interferometry differs from spectrophotometry in two major areas. First, in interferometry the radiation is not dispersed into monochromatic frequencies but rather the radiation is modulated by means of a vibrating mirror. The modulation process results in an interferogram that in itself does not give very much information. However if the interferogram is fed into a wave analyzer, spectral information can be extracted. Another difference between spectrophotometry and interferometry is in the physical form of the entrance aperture. In a spectrophotometer the energy enters through narrow slits, just a few tenths of a millimeter wide. In an interferometer the energy enters through a window over an inch in diameter. Consequently, the amount of energy available to the detector of an interferometer is orders of magnitude greater than that available to the detector of a spectrophotometer.

These differences give rise to the main advantage of an interferometer, sensitivity. A secondary advantage is scanning speed. A complete interferogram can be recorded in a little over a tenth of a second although more typical scanning speeds are in the order of second.

These characteristics make the interferometer first choice for anyone interested in infrared emission.⁽²⁾ Some of the possibilities of infrared emission spectroscopy are that samples can be scanned "in situ" with no need of disturbing the sample. This ability could save considerable sample handling in a process-control type of analysis or make analysis of hazardous materials more feasible. Infrared emission spectroscopy is completely non-destructive to the sample and could be used in the analysis of such things as valuable oil paintings. Interferometry can also be used to analyze samples too big for conventional spectrophotometers; for example, our atmosphere in air pollution studies. And it can be used to analyze samples too small; for example, pesticide residue on plant growth.

Experimental

The heart of the interferometer is the optical head. The head is fairly small, about 3 x 6 x 7 inches and is readily portable. The head is connected to the control panel by a ten-foot cable. The aperture is 1-1/4 inches in diameter and has a field of view of eighteen degrees. No special optics are required to get the sample's radiation to enter the optical head; you simply point the aperture at the sample. Unwanted radiation from material in the field of view can be masked out with aluminum foil. The foil being very reflective has essentially zero emissivity.

The head is also readily adapted to a mirror-type telescope making it possible to analyze samples at a remote distance. Smoke has been reportedly analyzed from stacks up to one-half mile away.⁽³⁾

Figure 1 is a diagram of the optical head. The interferometer is of the Michelson type. Radiation incident on the window passes into the optical head and strikes the beam divider. Here the radiation is split into two beams; one beam traveling to a stationary mirror and returning and the other beam traveling to a vibrating mirror and returning. Upon reaching the beam divider, the two beams unite and are reflected to the detector, a thermister bolometer. Some energy is lost exiting out through the entrance aperture.

The position of the vibrating mirror when both beams have the same path length is called the zero position. Consider for the moment that the incoming radiation is monochromatic. At the mirror's zero position, all waves will arrive at the detector in-phase giving a maximum signal. As the mirror moves infinitesimally in either direction from its zero position the relative path lengths of the two beams will change and all the waves will not arrive at the detector in-phase. Destructive cancellation will result and the detector's output will be diminished. When the mirror has moved $1/4$ wavelength away from the zero position the total path difference will be $1/2$ wavelength, and complete cancellation of the beam will result giving a minimum output from the detector. As the mirror continues to move away, the signal will start to increase until at mirror position $1/2$ wavelength away from zero position, the retardation will be one full wavelength and all waves will be in-phase again. The detector output at this point will be a maximum equal to the first maximum. As the mirror continues to travel maxima are reached every even quarter wavelength from the zero position and minima are reached every odd quarter wavelength. The continuous output then is a sine wave. The frequency of this sine wave is related to the monochromatic input radiation by the equation:

$$f = L/T \times 1/\lambda$$

Where L is the length of the mirror's repetitive travel in microns and T is the time in seconds. λ is in microns. For most of our work L is 500 microns and T is one second. Thus, 2 micron radiation would give rise to a 250 cycles/sec audio sine wave. A wavelength of 16 microns would result in a 31 cycles/sec sine wave. Hence, all the frequencies in the interferogram of radiation between 2 to 16 microns can be found in the audio range below 250 cycles/sec. The length of the mirror's path also determines the resolution of the interferometer. The longer the path length the better the resolution. Our normal resolution is 20 cm^{-1} , the reciprocal of the path length.

Figure 2 shows the sawtooth nature of the mirror's travel and the resulting interferograms. Note that the return time for the mirror is very short and that the mirror's travel is very linear. The interferograms shown are not of monochromatic light.

To visualize what happens when polychromatic radiation enters the interferometer is a little more difficult. At the mirror's zero position, all the frequencies will still be in-phase and a maximum output of the detector will be obtained. However, as the mirror moves away from the zero position destructive cancellation occurs diminishing the output but not in the regular fashion of a sine wave. The result is a very sharp peak at the mirror's zero position with highly damped side bands.

One of the major drawbacks to interferometry is that it is impossible to recognize a spectrum from the interferogram; the interferogram must be filtered to obtain the spectrum. The filtering may be done in several ways. The interferogram can be fed repetitively into a variable filter or wave analyzer. The wave analyzer is set for the first audio frequency and a signal is recorded that is proportional to the amount of that frequency present in the interferogram. The wave analyzer is automatically advanced to the next audio frequency and its signal recorded. As this process is continued the spectrum is recorded.

Alternatively the interferogram may be mathematically filtered by means of the Fourier transformation. The equation for this transformation is:

$$G(\nu) = \int_0^{\infty} I(x) \cos 2\pi \nu x dx$$

where $G(\nu)$ is the intensity of the spectrum

$I(x)$ is the intensity of the interferogram

ν is the frequency in wave numbers

x is the path difference in cm

A rather novel way of filtering the interferogram is to transfer the data to a photographic film and place it in a laser beam. Lenses can then be used to optically perform the Fourier transformation and the image recorded on another piece of film.

Results

Figures 3a and 3b show a comparison between an absorption spectrum as recorded by a spectrophotometer and an emission spectrum derived from an interferogram. The spectra are very similar but not identical. The differences are primarily in resolution and relative intensities.

The effect of temperature on the emission spectrum of beta-hydroxyethyl acetate is shown in Figure 4. The spectrum is of course more intense at the higher temperature but otherwise they are very similar. The carbonyl band near 1700 cm^{-1} is relatively more intense in the hotter spectrum and this is consistent with the Boltzmann distribution giving the higher energy levels a greater population in the hotter sample. To obtain these spectra, the acetate was poured onto a piece of aluminum foil and then allowed to drain. The thin film that remained on the foil was sufficient to give the observed results. The foil was heated by conduction.

One of the major problems of infrared emission spectroscopy is shown in Figure 5. The subject is the emission spectrum of "Saran". The bottom spectrum is of one single layer of "Saran" and shows good band structure. However, with four layers of "Saran" all of the band structure between 800 and 1500 cm^{-1} completely disappeared and we have recorded essentially the spectrum of a black body. This phenomenon is attributed to self-absorption.

Interferograms of samples which have a temperature within a few degrees of the detector's temperature are very noisy because of the low signal level. In these cases, it is necessary to time average or co-add several hundred interferograms to obtain a satisfactory spectrum.⁽²⁾

Conclusion

An infrared interferometer covering the region 2-16 microns is seen as a potential tool for the practical spectroscopist. It does not have the universal applicability of the more conventional infrared techniques but its unique characteristics of high sensitivity, rapid scanning, and portability will certainly be used to solve specific problems that would be otherwise difficult if not impossible to solve.

(1) L. C. Block and A. S. Zachor, Appl. Optics 3, 209 (1964).

(2) M. J. D. Low and I. Coleman, Spectrochimica Acta 22, 369 (1966).

(3) Chemical and Engineering News 45, No. 7, 54 (1967).

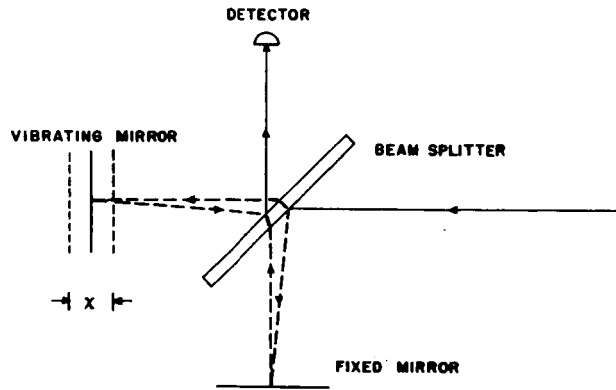


Figure 1. OPTICAL HEAD

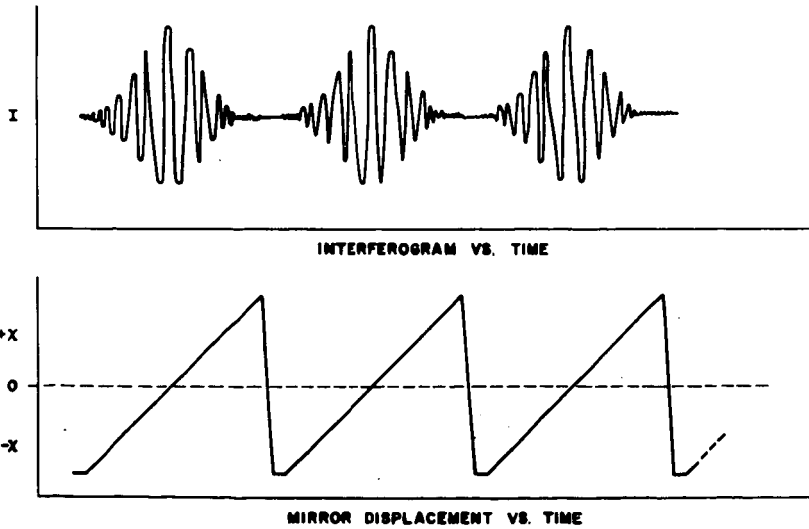


Figure 2. MIRROR TRAVEL AND RESULTING INTERFEROGRAM

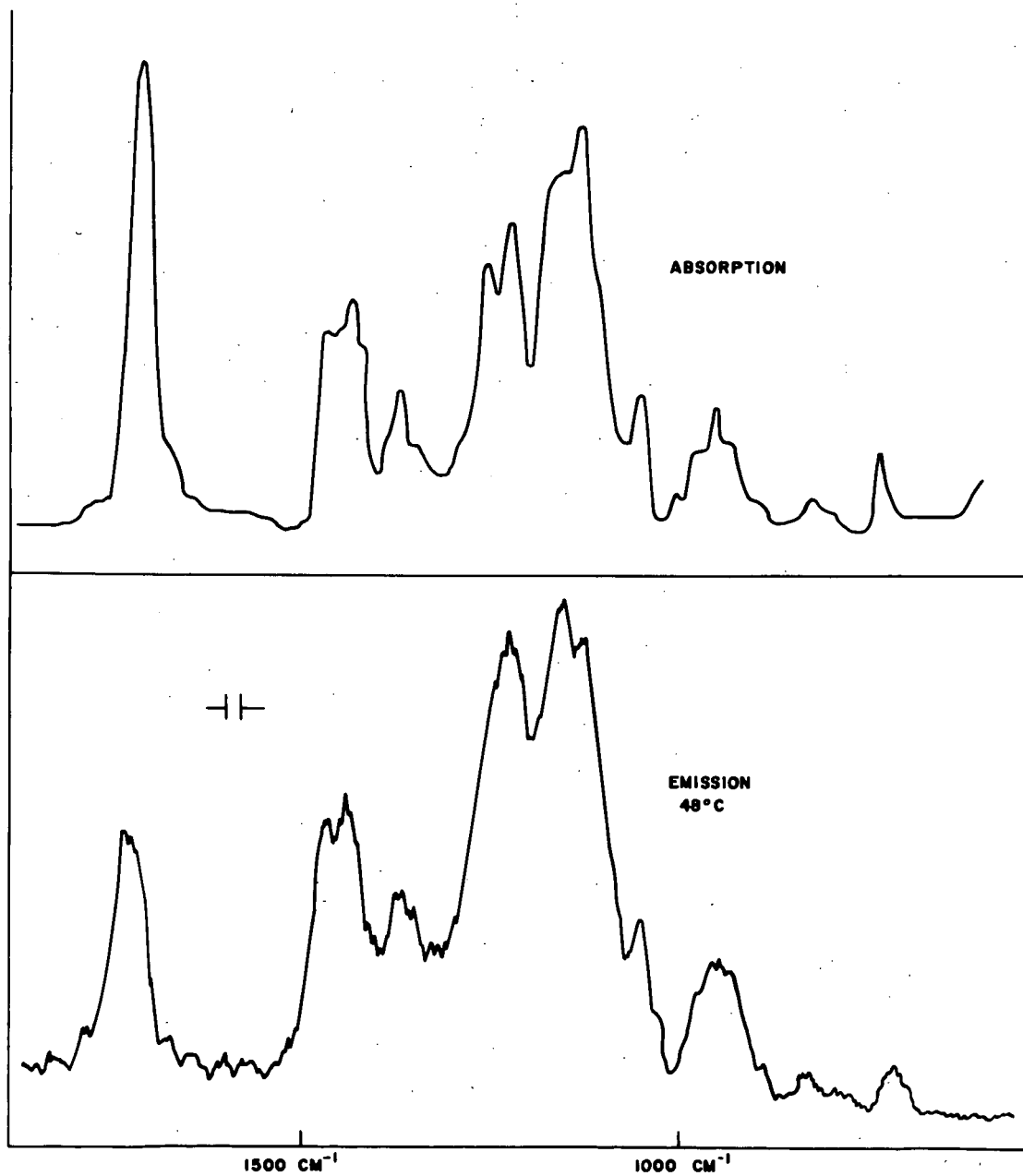


Figure 3a. and 3b. INFRARED SPECTRA OF "KRYLON"

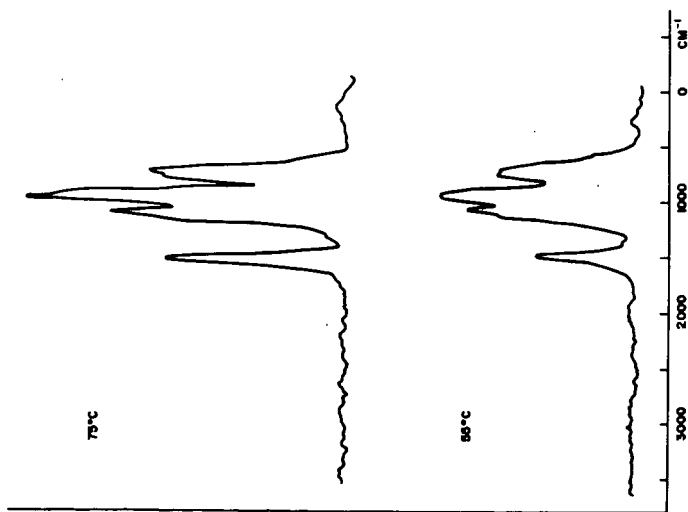


Figure 4. EMISSION SPECTRA OF
 β -HYDROXYETHYL ACETATE

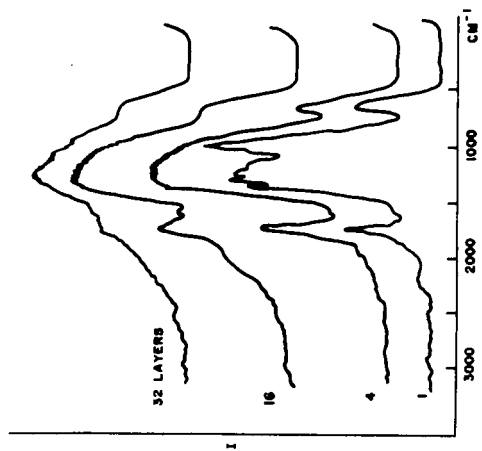


Figure 5. EMISSION SPECTRA
OF "SARAN"